STUDIES OF C60, C70 AND OTHER FULLERENES:

SYNTHESIS, DERIVATIZATION, ELECTROCHEMISTRY,

LUBRICANT PROPERTIES AND NEW COMPOSITE MATERIALS

FINAL REPORT

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and M.A. Ciufolini

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New designs for fullerene generators have been developed, including systems for producing endohedral species with metals inside the C_{60} or C_{70} cages. Also, focussed solar energy has been utilized for fullerene production. Electrochemical studies have led to the identification of C_{60}^{-1}, C_{60}^{-2} ...C_{60}^{-6} ions and utilized for preparation of super-conducting K_3C_{60}. Birch reductions of C_{60} and C_{70} led to $C_{60}H_{30}$ and $C_{70}H_{30}$ respectively. Adducts of C_{60} with tetraphenylcyclopentadienone and with cyclopropananaphthalene are described, and low-temperature reactions of C_{60} with H_2 and with energetic nitroben ion beams are reported. C_{60} does not appear to enhance the lubricity of motor oil formulations. The vapor pressure has been measured and it is estimated that the total pressure reaches one atmosphere at ca. 1523K.

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INTRODUCTION

The goal of this research was to investigate various materials applications, materials properties and the chemistry of the newly available soccer ball-shaped buckminsterfullerene, C$_{60}$, and related substances ("fullerenes"). We proposed to explore research areas that could lead to important advances in materials science, energy technology, and, possibly, even in biomedicine. The results of this research effort at Rice University are documented in the Ph.D. theses of 10 students (6 more in progress) and in many publications, including a definitive book edited by W.E. Billups and M.A. Ciufolini. In the various sections of this report and the related publications, we describe advances in the preparation and characterization of fullerenes and metal endohedral fullerenes; the electrochemical synthesis of superconducting fullerides; chemical reactions of fullerenes with hydrogen, helium, and organic molecules; and measurements of vapor pressures, lubricity and other properties.

1. <u>Fullerene Generator Development</u> (Richard E. Smalley and Associates).

Since the original discovery in 1985 that fullerenes are produced spontaneously in laser-generated carbon vapors,[1] extensive research has been devoted to finding ways of making these species in large amounts at high yield. Triggered 5 years later by the success of Kratschmer et al.[2] in producing the first milligram amounts by resistive heating of graphite in an atmosphere of helium, the manufacture of these new materials has now

become something of a cottage industry. Even with subsequent improvements using carbon arcs, production of fullerenes remains a highly expensive process which has resisted all attempts to scale-up beyond several tens of grams per hour. This figure applies to the most abundant fullerenes, C_{60} and C_{70}. Higher fullerenes are produced by current techniques in very small amounts and they are even more expensive.

Buckminsterfullerene (C_{60}) has now been prepared in multigram quantities by contact arc vaporization of a graphite rod in a 100-Torr atmosphere of helium, followed by extraction of the resultant graphitic soot with toluene. The dominance of C_{60} in this extract has been verified by mass, FTIR and NMR Spectroscopy.[3,4]

In the course of an extensive series of experiments aimed at increasing the production of both empty fullerenes and endohedrally doped metallofullerenes, Smalley and Chibante[5] may have discovered the principal mechanism which has prevented efficient scaling of the carbon arc technique to large rod sizes, i.e., photochemical destruction of the fullerenes by light from the arc. After considering ways this problem can be overcome in a fashion that scales well to large rod sizes, they proposed that the best answer may also be the simplest: sunlight. A solar furnace has been successfully used for C_{60} preparation.[5]

2.   Metal Endohedral Fullerenes (Richard E. Smalley and Associates).

By operating the carbon arc in a temperature-controlled flowing environment, fullerenes remain in the gas phase and condense on cold surfaces downstream. By using metal-doped graphite electrodes in such a configuration, and by providing a filtering medium, metallofullerenes can be extracted from the non-sublimable soot. Deposition onto a retractable collection surface allows these materials to be transported from the apparatus without ever contacting air or moisture. By vacuum distilling away the empty fullerenes, one can produce metallofullerenes without the use of solvents while maintaining an inert environment. Characterization and utilization of these unique materials is now feasible.

Macroscopic quantities of fullerenes with a metal atom inside were first produced for lanthanum by laser vaporization of a La_3O_3/graphite composite rod in a high-temperature tube furnace.[6] In the sublimed film, $La@C_{60}$, $La@C_{70}$, $La@C_{74}$, and $La@C_{82}$ were all present, while $La@C_{82}$ was found to be abundant and uniquely soluble in toluene. Many rare earth elements have been found to be readily trapped inside fullerenes with one or more atoms both by the laser vaporization/high temperature furnace technique and by the carbon arc technique.

Recently, the electronic structure of $Ca@C_{60}$ in the gas phase[7] was probed by ultraviolet photoelectron spectroscopy (UPS) of $Ca@C_{60}^-$. The electron affinity of $Ca@C_{60}$ was found to be 3.0 eV. The spectrum suggests that Ca donates its two 4s electrons to the $C_{60}I_{1u}$ LUMO. Ab initio self-consistent field Hartree-Fock calculations. were performed on $Ca@C_{60}$ at four different symmetries, I_h, D_{3d}, D_{5d}, and C_{5v}. It was found that the C_{5v} symmetry has the lowest energy with the central Ca^{2+} ion 0.7 A away from the center of C_{60} and that $Ca@C_{60}$ has a $^3A_2$ triplet electronic ground state in C_{5v} symmetry.

3.   Electrochemical Syntheses of Superconducting Fulleride-Derived Materials (Lon J. Wilson and Associates).

In November of 1990, we reported the first electrochemical reduction of C_{60} to the C_{60}^- and C_{60}^{2-} ions in solution.[3] Subsequently, electrochemical reductions to the C_{60}^{3-}, C_{60}^{4-}, C_{60}^{5-}, and C_{60}^{6-} anion levels[8-11] were also reported. Shortly thereafter, this observed production of fulleride ions in solution by electrochemistry took on new importance with the discovery that K_3C_{60} (containing discrete C_{60}^{3-} ions) formed a metallic superconducting phase with $T_c = 18$ K.[12] Our DARPA-sponsored research has explored the possibility of using electrochemistry to electrosynthesize and electrocrystallize superconducting salts of C_{60}^{3-} from solution. An electrosynthetic approach to such superconducting materials has potential advantage over chemical vapor deposition (CVD) methods in that pure, single-phase materials are often obtained by electrosynthetic methods and large single crystals also often result from electrocrystallization techniques. Our methods and initial results are documented below. A recent publication describing these results in more detail is also available.[13]

Electrochemistry of C_{60}

C_{60} reduction processes. Electrochemical analysis of C_{60} reveals the existence of at least eight oxidation states, (C_{60}^n: $n = 0$, -1, -2, -3, -4, -5, -6, and +x, where x has yet to be definitely established) by use of cyclic voltammetry and differential pulse polography. The six known reductions of C_{60} are all reversible by cyclic voltammetry at -10°C as shown in Figure 1. Historically, these six reduction processes for C_{60} were uncovered literally "one electron at a time" with the two-,[3] three-,[8,9] four- and five-[10] and finally six-electron[11] processes being reported.
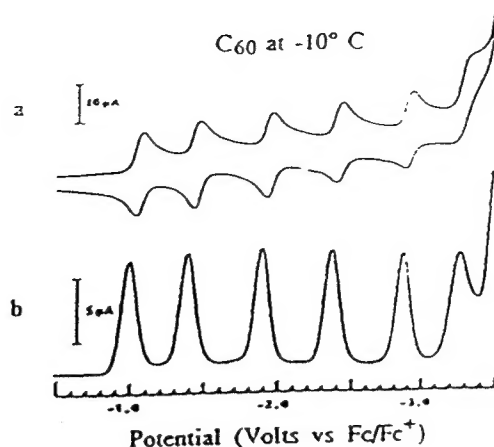
C60 at -10° C

Potential (Volts vs Fc/Fc+)

Figure 1. Reduction of C_{60} in CH_3CN/toluene at -10 °C using (a) cyclic voltammetry at a 100 mV/s scan rate and (b) differential pulse voltammetry (3 mm dia. glassy carbon working electrode, 50-mV pulse, 50-ms pulse width, 300-ms period, 25 mV/s scan rate). Reprinted with permission from Reference 4.

All six electrochemical reductions of Figure 1 are reversible at a scan rate of 100 mV s^{-1} in a CH_3CN/toluene solvent system at -10°C. Even more remarkable, the reductions occur at fairly evenly-spaced potentials ($ca. \Delta 200$ mV). Initial M.O. calculations on C_{60} predicted a triply-degenerate LUMO (lowest unoccupied molecular orbital) of t_{1u} symmetry,[14] and the observed electrochemistry of C_{60} supports this view.

Other solvents such as THF or CH_2Cl_2 reveal less reversible electrochemical behavior, especially for the more negative reduction processes.[8] Bulk electrolysis in benzonitrile verifies the first four reductions of C_{60} as one-electron transfers.[10a] The C_{60}^-, C_{60}^{2-}, and C_{60}^{3-} fulleride ions remain stable in benzonitrile for up to several days, and neutral C_{60} is quantitatively recovered from these solutions after reoxidation. Epr spectroelectrochemical studies of these fulleride ions in frozen solution indicated $S = 1/2$ ground states for C_{60}^- and C_{60}^{3-} and an $S = 1$ ground state for the C_{60}^{2-} ion.[14] C_{60}^{4-} has so far only been produced by bulk electrolysis in either benzonitrile or pyridine using the wide reduction windows of these solvents, however, quantitative recovery of C_{60} was not achieved upon reoxidation of the C_{60}^{4-} solutions.[15]

Electrosynthesis of K3C60

The discovery of conditions under which all six reductions of C_{60} are reversible at slow scan rates indicated that the $C_{60}^- \rightarrow C_{60}^{6-}$ anions could be generated in bulk by controlled-potential electrolysis (CPE),[10] and we initiated such studies and selected K_3C_{60} as an initial target compound because of its superconducting properties. Previous syntheses of superconducting K_3C_{60} employed a chemical vapor deposition (CVD) approach, but we believe that an electrosynthetic method offers real advantages over CVD.

Specifically, we anticipated being able to prepare literally gram quantities of crystalline K_3C_{60} and hopefully to grow large single crystals from solution in order to directly measure electrical transport properties (*e.g.*, current density) in single crystals. By comparison, a CVD synthetic approach offers less hope of obtaining large single crystals for such measurements. Finally, an electro-synthetic approach also offers the prospect of producing new materials such as K_nC_{60} (with n = 1) and K_2C_{60} (with n = 2), whereas these less-highly-reduced phases of C_{60} have remained elusive with high-temperature CVD syntheses.

After much trial and error, we settled on a solvent/electrolyte system of CH_3CN/KPF_6 for our electrosynthesis of K_3C_{60}. A flow diagram of the synthesis is shown in the Figure 2 where the potential is held at -1.6 V (*vs.* Ag/AgCl) during the electrolysis at 40 cm^2 Pt gauze working electrode. The advantage offered by the CH_3CN/KPF_6 system is that only the K_3C_{60} product crystallized from the bulk solution, leaving the supporting electrolyte (KPF_6) in solution as a clean method of separating K_3C_{60} from KPF_6. Finally, washing the solid K_3C_{60} with toluene removed any unreduced C_{60} from the product. These preliminary results indicate that an electrosynthetic approach to fulleride-based materials should be a general success. Electrocrystallization
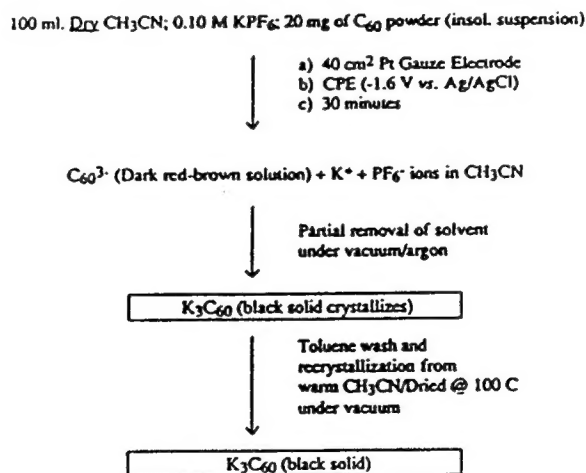
100 ml. Dry CH_3CN; 0.10 M KPF_6; 20 mg of C_{60} powder (insol. suspension)

a) 40 cm^2 Pt Gauze Electrode
b) CPE (-1.6 V vs. Ag/AgCl)
c) 30 minutes

C_{60}^{3-} (Dark red-brown solution) + K^+ + PF_6^- ions in CH_3CN

Partial removal of solvent
under vacuum/argon

K_3C_{60} (black solid crystallizes)

Toluene wash and
recrystallization from
warm CH_3CN/Dried @ 100 C
under vacuum

K_3C_{60} (black solid)

Figure 2. Flow Scheme for the Electrosynthesis of K_3C_{60} from C_{60}.

attempts are continuing for K_3C_{60} and other C_{60}^{3-} materials, and when large single crystals become available, their superconducting properties will be characterized and compared to the crystalline phases obtained by CVD methods. We hope to have such crystals soon.

4.   Birch, Reduction of C_{60} and C_{70} (W.E. Billups and Associates).

The isolation of buckminsterfullerenes C_{60} and C_{70}[1,16] in bulk quantities[2,5,16] has led to a flurry of activity directed at the chemical modification of these new materials. The objective of this research was the development of a process for the production of fullerene hydrides to be used as hydrogen storage materials. In principle, it should be possible to store 30 moles of dihydrogen per mole of C_{60}. However, $C_{60}H_{60}$ is a highly energetic compound and it has not been possible to prepare this fully reduced material using conventional chemistry.

In this study, we have investigated the Birch reduction of C_{60} as a route to new fullerene hydrides. The major product formed in the Birch reduction of C_{60} is a species in which 36 hydrogen atoms are bound chemically to the carbon skeleton. Although mass spectral analyses are inconclusive with regard to other hydrides that are formed during the Birch reduction, there is evidence for $C_{60}H_{18}$ as well as $C_{60}H_{28}$ and $C_{60}H_{32}$. The mass spectrum recorded under FD conditions is shown as Figure 3. The peak at m/e 755.6 corresponds to $C_{60}H_{36}$.

A mechanism which would account for the formation of $C_{60}H_{36}$ is shown in the scheme presented below.
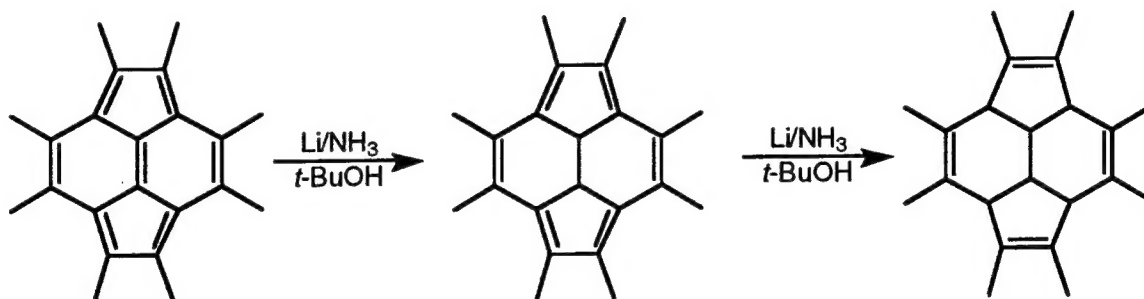
It is interesting that 36 is the number of hydrogen atoms required to leave a single, non-conjugated double bond in each of the 12 cyclopentane subunits of C_{60}. A possible structure of this product is presented as Figure 4.

Figure 3

FDMS of the Birch Reduction of 99% C_{60}

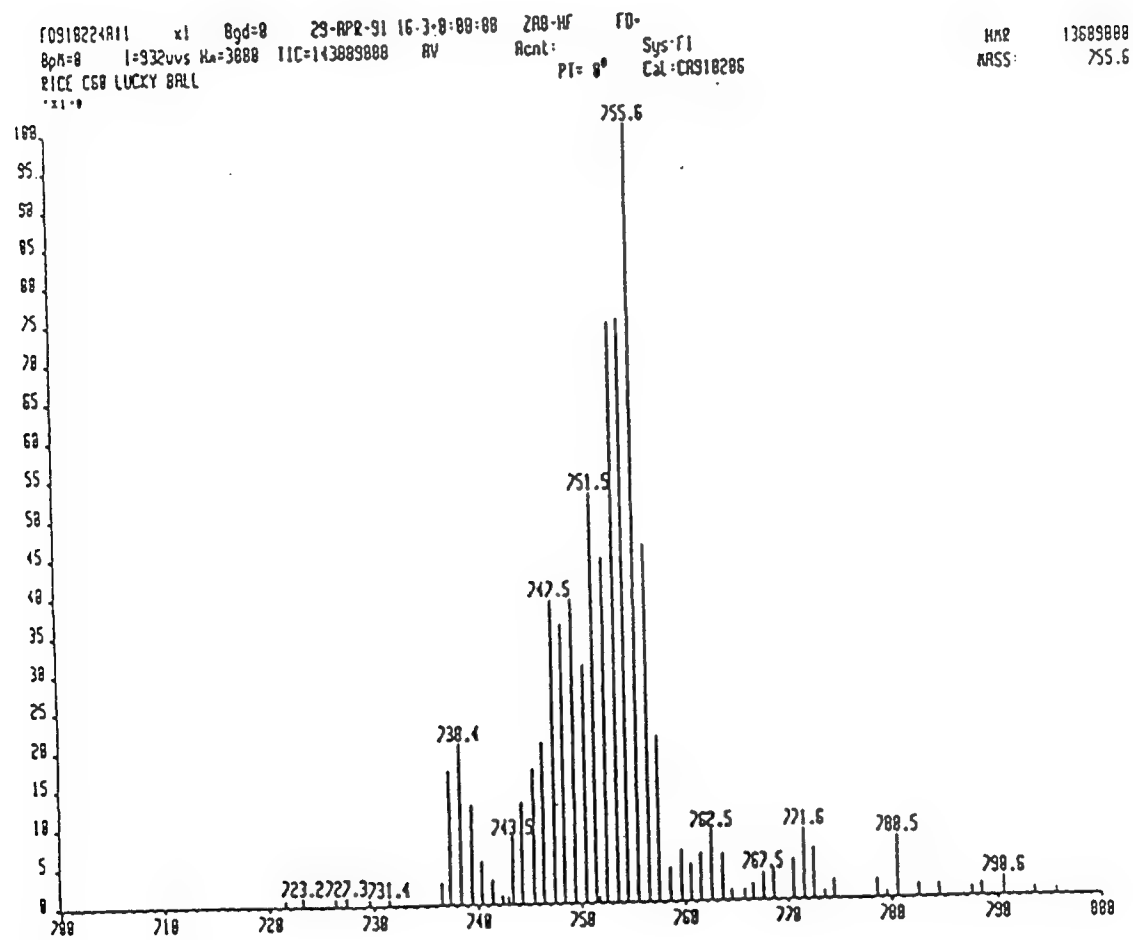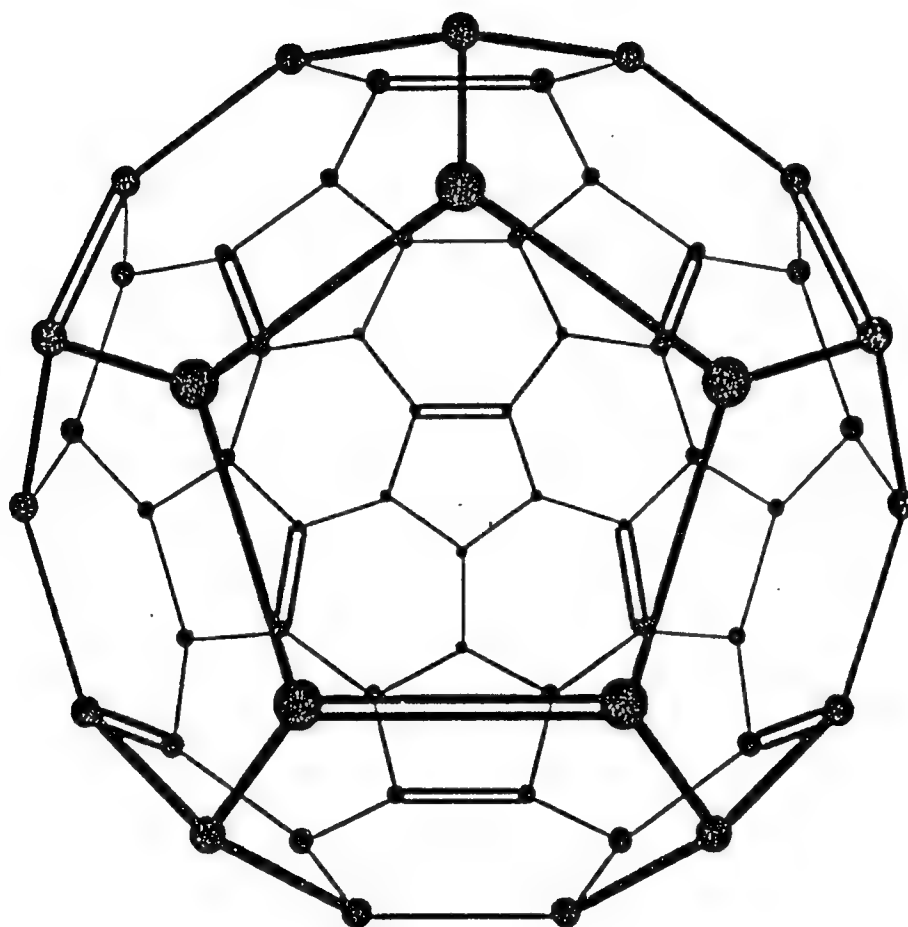calibration shifted -0.5 amu, $C_{60}H_{36}$ = 756 amu

Figure 4

Structure of $C_{60}H_{36}$ from the Birch Reduction of C_{60}

Treatment of a toluene solution of the Birch-reduced product with dichlorodicyanoquinone (DDQ) led to the rapid formation of the starting fullerene C_{60}. Thus, the reduction of C_{60} is fully reversible. This facile activation of the C-H bonds of $C_{60}H_{36}$ is consistent with theoretical calculations dealing with the fullerene hydrides.[16]

$$C_{60} \underset{DDQ}{\overset{Li/\textit{t}\text{-BuOH/NH}_3}{\rightleftarrows}} C_{60}H_{36}$$
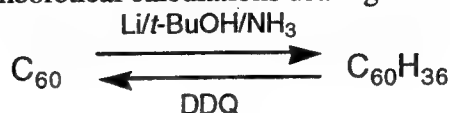
Due to the limited availability of C_{70}, the chemistry of this fullerene has been somewhat less developed; however, we have isolated enough C_{70} (95% purity by HPLC) to demonstrate that the Birch reduction of C_{70} using Li metal in liquid ammonia and t-butyl alcohol yields a nearly white solid which also darkens irreversibly to a beige colored material upon exposure to the atmosphere. Analysis of this material by FDMS showed that the major product was $C_{70}H_{36}$, in strict analogy to the Birch reduction of C_{60} under the same reaction conditions. Since both fullerenes contain 12 cyclopentanoid rings it seems reasonable that a similar mechanism accounts for both results. Treatment of a benzene solution of the reduced fullerene with DDQ for 5 hr at room temperature afforded a quantitative yield of the starting fullerene, as monitored by HPLC. Thus the reduction of both fullerenes appears to be fully reversible.

$$C_{70} \underset{DDQ}{\overset{Li/\textit{t}\text{-BuOH/NH}_3}{\rightleftarrows}} C_{70}H_{36}$$
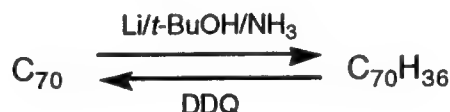
Calculations by Dr. Gus Scuseria suggest that the structure presented as Figure 5 may depict the most stable form of $C_{70}H_{36}$.

If the dihydrogen (18 moles per mole of C_{60}) contained in these Birch products could be removed both easily and reversibly, then these Birch products might provide a method to safely store hydrogen as a fuel source. It has been demonstrated that the Birch products of C_{60} and C_{70} may be removed by oxidation with DDQ, but this type of reaction would be impractical for a fuel storage device. One of the first observations made about the Birch products of the fullerenes is their relative instability, as evidenced by the rapid color change from white to beige to yellow upon exposure to air or heat. Therefore, it was decided to investigate the thermal behavior of the Birch product of C_{60} by thermo-gravimetric analysis (TGA) to determine the decomposition pattern of the product.

Figure 5

Structure of $C_{70}H_{36}$ from the Birch Reduction of C_{70}
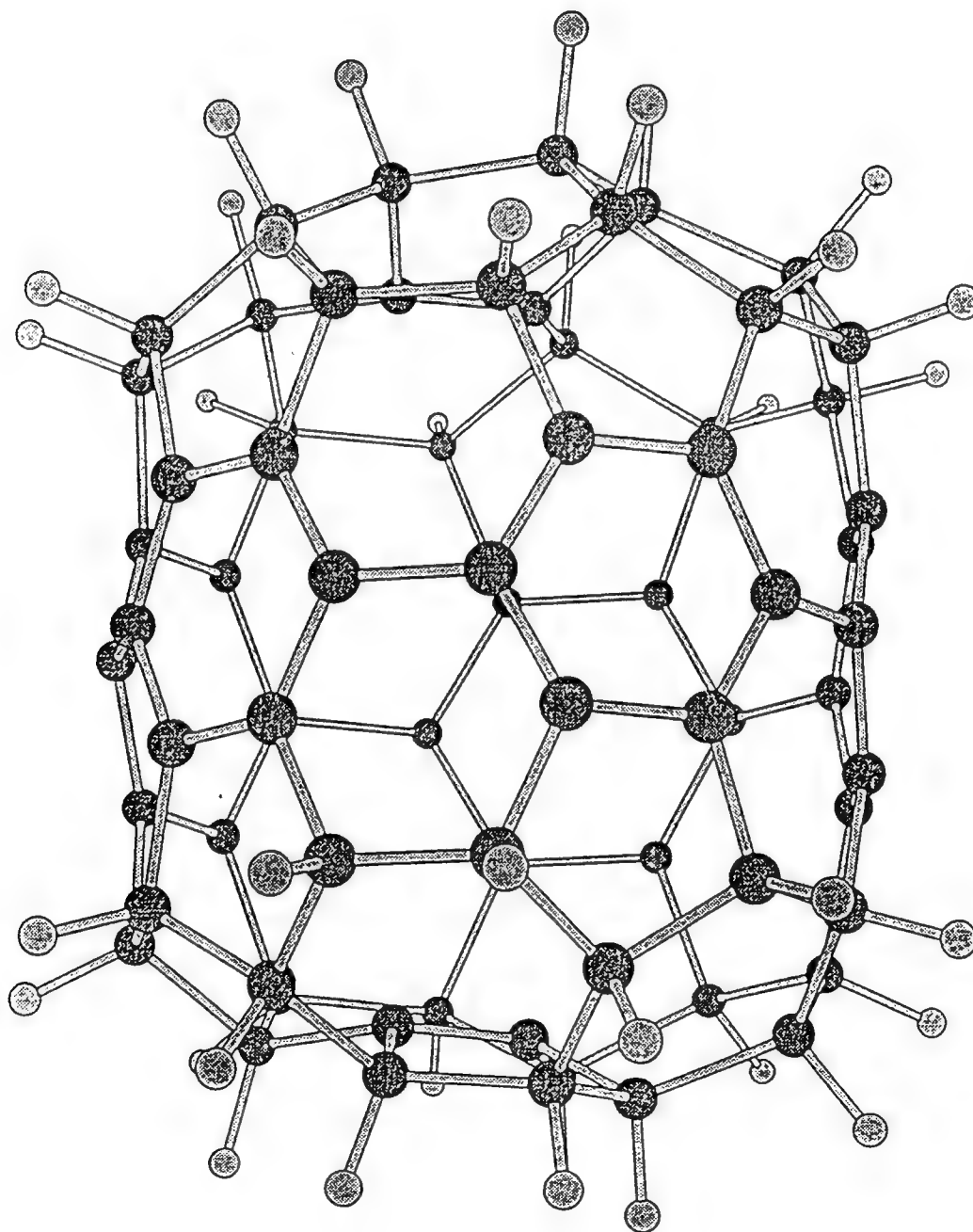
The constraints of time have prevented detailed studies of the thermal behavior of these materials. However, some preliminary investigations using thermo-gravimetric analysis of Birch reduced C_{60} from 25-800 °C at 5 °C/min under an argon blanket showed a 7% weight loss from 25-110 °C, a 6% weight loss from 120-260 °C, and finally a 43% weight loss from 300-750 °C. The weight loss of 7% from 25-110 °C is greater than would be expected for a simple loss of dihydrogen. If only hydrogen had been removed from the Birch product, the weight loss would have been 5%. This product had been dried *in vacuo* for 24 h, and TGA of pure C_{60} dried in this manner verified that the technique was effective for removing detectable residual solvents from the sample. Since the TGA instrument employed was not equipped for the analysis of outgases (gaseous decomposition products), this study is still inconclusive and the determination of the products produced during this process will be a long tedious task.

The characterization of these fullerene hydrides has presented a major obstacle during this investigation. As indicated above, FDMS shows a range of peaks with the major one at the position expected for $C_{60}H_{36}$. At the moment, we not able to determine whether these peaks correspond to discrete compounds or whether they are fragment peaks. We believe that some of the problems associated with characterization of these materials can be solved using $^3He@C_{60}$.[17,18,19]

5.   Adducts of C$_{60}$

(a) Diels-Alder Reaction (J. L. Margrave, V. N. Khabashesku and R. H. Hauge)

We have studied the Diels-Alder [4+2] cycloaddition reaction of tetraphenylcyclo-
pentadienone (TPC) to fullerene C$_{60}$ with the aim of getting a new hard carbon material,
which might be accessed by further cross-linking polymerization of the product 1, obtained
via thermal or photochemical elimination of CO molecule from [C$_{60}$·TPC] adduct. The
reaction is shown as follows:
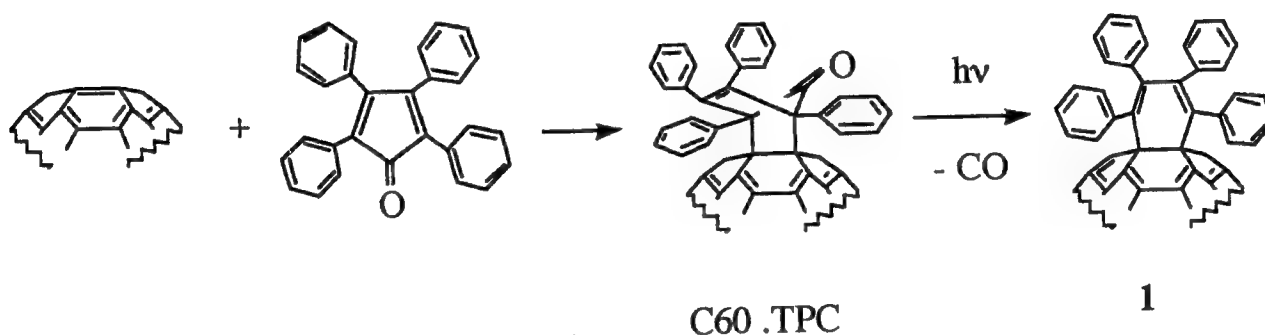
C60 .TPC   1

To date we have succeeded in isolation of milligram quantities of the C$_{60}$·TPC adduct
by liquid chromatography with spectroscopic characterization of this new compound by
^{13}C NMR (Fig.6), UV-Vis (Fig. 7), IR (Fig. 8) and FAB MS (m/z 1104; M^{+}) techniques.
A similar synthesis of the [4+2] adduct of isobenzofuran to fullerene C$_{60}$ was published
by F. Wudl and coworkers.[20]

Large scale synthesis of the [C$_{60}$·TPC] adduct as well as studies of [4+2]
cycloaddition of C$_{60}$ to a-pyrone are now in progress. Our thin film deposition studies
have shown some molecular hydrogen adsorption by neat C$_{60}$ and nickel doped C$_{60}$ films.
To understand the mechanism of this process, which may be caused by initial molecular
hydrogen complexation or a bond insertion hydrogenation of C$_{60}$·metal complexes, matrix
isolation spectroscopic studies are now under way.
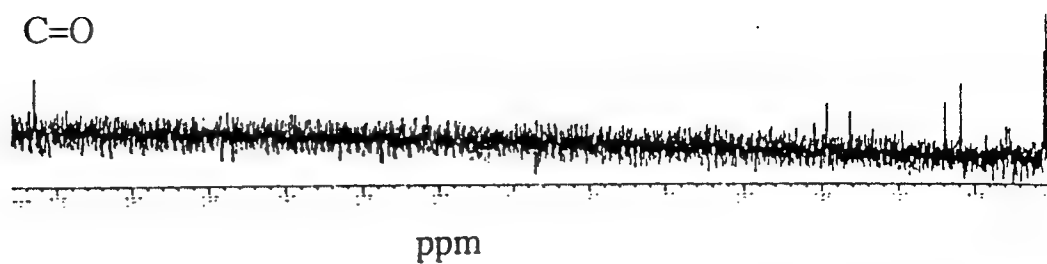
C=O

ppm

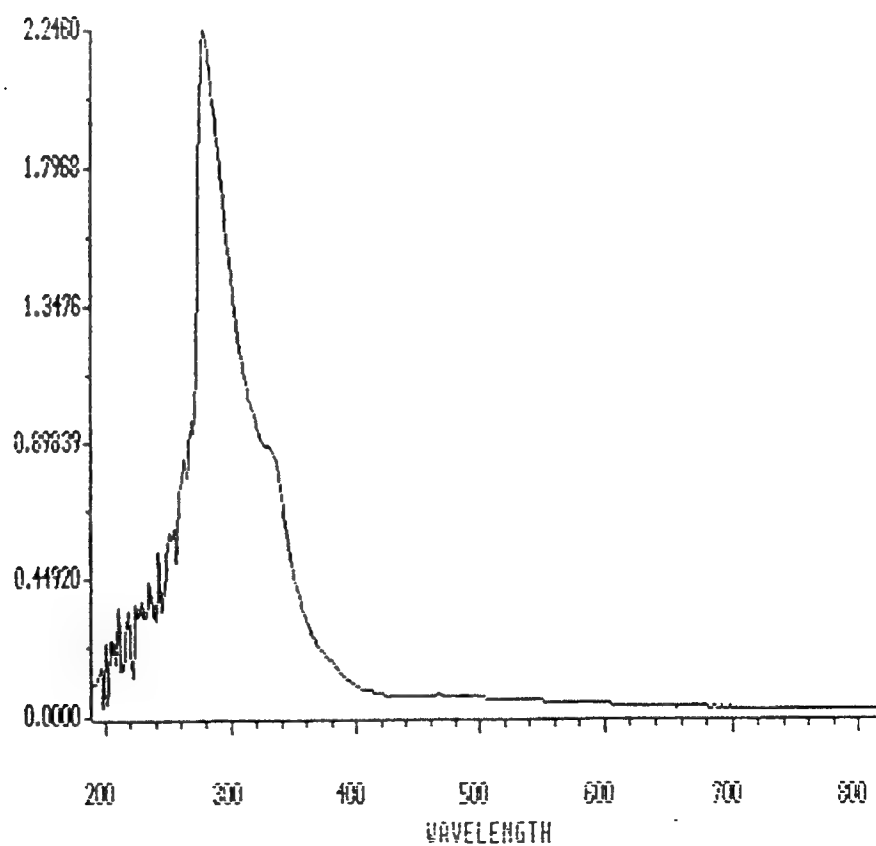Figure 6. ^{13}C NMR spectrum of C_{60}·TPC adduct in C_6D_6.

Figure 7. UV-vis spectrum of C_{60}·TPC adduct in benzene solution (solvent is subtracted).
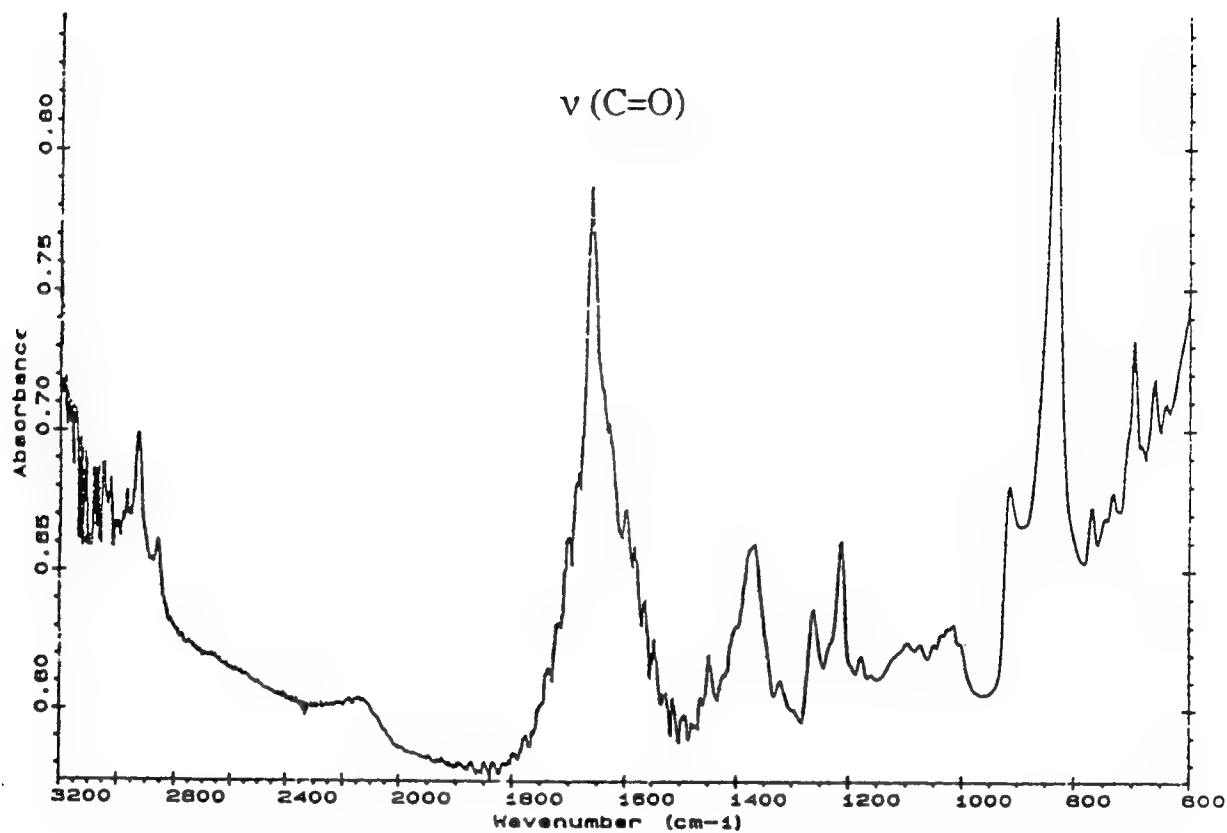
Figure 8. IR spectrum of $C_{60} \cdot$TPC adduct pressed into KBr pellet.

5.　　Adducts of He@C_{60} (W.E. Billups and Associates).

The recent discovery that ^{3}He can be introduced into the fullerenes C_{60} and C_{70} by heating at 620°C with the helium at high pressure represents an important advance in the characterization of fullerene derivatives since the ^{3}He NMR spectrum of each product should yield a single sharp peak and no non-fullerene products or impurities would give signals.[17-19] The feasibility of using this technique was demonstrated by carrying out a simple reaction in which a diradical was condensed with ^{3}He@C_{60} (see Figure 9). We are currently carrying out the Birch reductions using ^{3}He@C_{60}. Examination of the ^{3}He NMR spectrum of our products should provide a good indication of the number of isomers produced in this reactions.

Figure 9

18

^{3}He NMR spectrum of the Reaction Product of C60 and Cyclopropanaphthalene
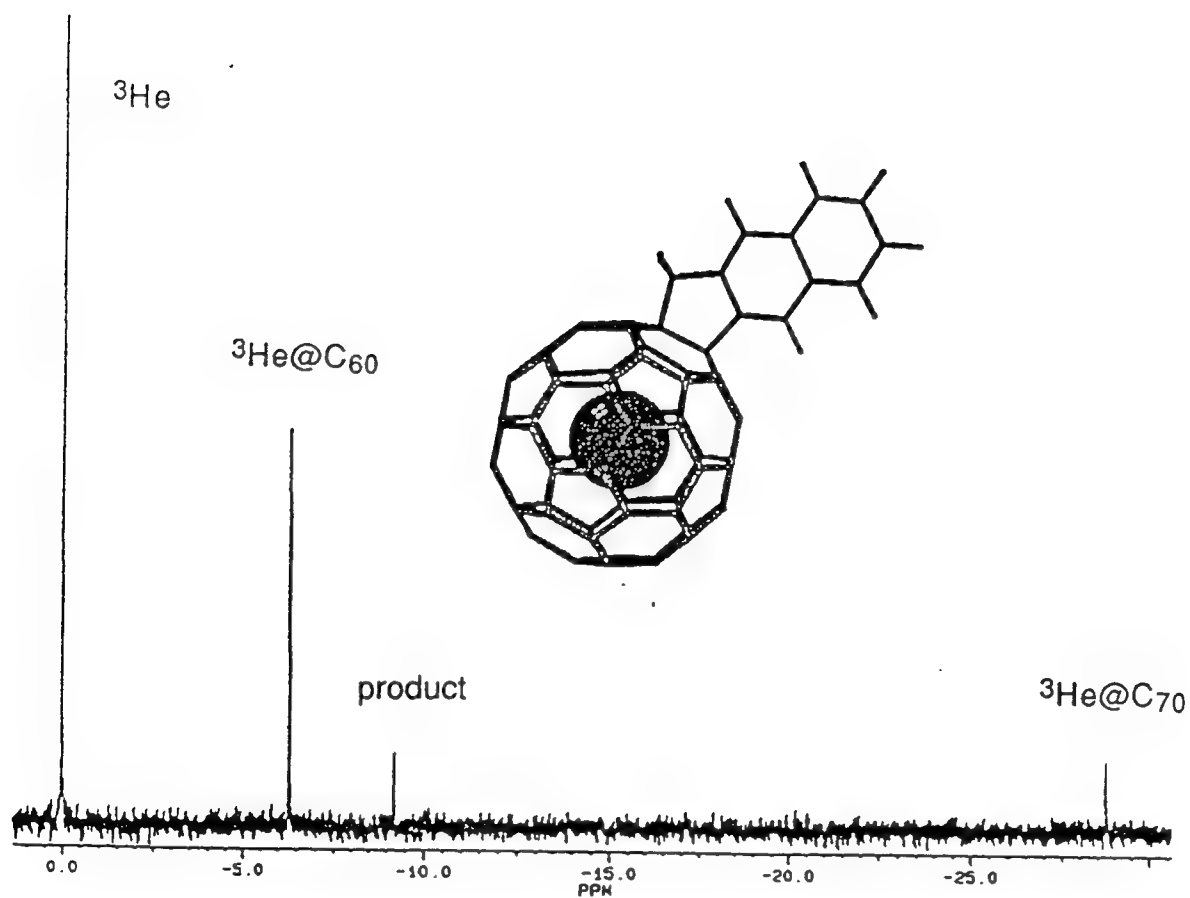
6.   Reactions of C_{60}-Thin Films with Hydrogen and with Nitrogen

Our thin film deposition studies have shown some molecular hydrogen adsorption by neat C_{60} and nickel doped C_{60} films at low temperatures. This process may be caused by initial molecular hydrogen complexation or a bond insertion hydrogenation of C_{60} metal complexes.

Both empirical and ab initio calculations[21] have shown that covalent carbon-nitrogen solids such as b-C_3N_4 may possess hardness comparable to diamond. Such predictions provide a strong reason for experimental efforts[22-24] to synthesize this superhard material. Such a material offers exciting prospects for new hard coating applications. Recently, C. Niu et al.[25] reported the synthesis of hard C-N films, containing up to 40 percent nitrogen. These films were prepared by laser ablation of graphite targets to produce carbon beams which were combined with atomic nitrogen from a radio frequency discharge source. The films were grown at substrate temperatures up to 800° C.

The goal of this work was to explore the possibility of growing hard carbon-nitrogen thin films at cryogenic temperatures. As a carbon source we have chosen the fullerene C_{60}, which can be vaporized by simple resistive heating at much lower temperatures than graphite. The films were prepared by co-deposition of a mixture of about 90% C_{60} and 10 % C_{70} with highly energetic nitrogen beams, created in a Kauffman ion source.[26] Both beams were directed at a Si wafer which is held at various temperatures from 300 down to 18 K. The nitrogen source was located inside a vacuum chamber such that the distance between the nozzle of beam focusing cone and the substrate was about 10-15 mm. Samples were deposited at a variety of nitrogen flux energies (from 300 to 700 V) and controlled C_{60} deposition rates (from about 500 to 1200 Å/hour). The deposits were studied by FTIR and Raman spectroscopy.

With the nitrogen beam present no C_{60} features remained in the spectra of all deposited films. This demonstrated complete chemical transformation of the fullerenes.

Formation of graphite was found to be the main process occurring at high C_{60} deposition rates (> 1000 Å/hour). At lower C_{60} deposition rates (~ 500 -600 Å/hour) we observed an increase of the amorphous carbon/graphite ratio as indicated by relative peak intensities in the Raman spectra. The nitrogen beam voltage was varied from 300 to 700 V and substrate temperature from 300 K (Fig. 10a down to 80 K (Fig. 10b).

Transformation of the C_{60} into a new nongraphitic material was observed at substrate deposition temperatures of 18-20 K . The Raman spectrum of this sample (Fig. 10c) did not show characteristic bands of C_{60} or those for amorphous carbon and graphite. The FTIR spectrum of the film deposited under the same conditions showed several new bands. None of those bands belong to the C_{60}/C_{70} precursor. Two of them, at 1030 and 1270 cm^{-1}, were located in 1000-1280 cm^{-1} C-N stretching vibrations range.

The above results demonstrate that energetic nitrogen atoms at cryogenic temperatures physically destroy fullerene molecules to form graphite or amorphous carbon at temperatures where molecular nitrogen does not condense. At lower temperatures (<30 K) where molecular nitrogen forms a film complete reaction of the deposited fullerene with nitrogen is observed. This strongly suggests that hard carbon films can be obtained by controlling the nitrogen deposition and reaction rate by simply controlling the substrate temperature. The use of high purity fullerene carbon beam sources, free of hydrogen impurities which are often found in graphite samples, along with a high purity nitrogen sources in a UHV system should be an excellent route to highly pure carbon-nitrogen films of variable stoichiometry with high nitrogen contents.
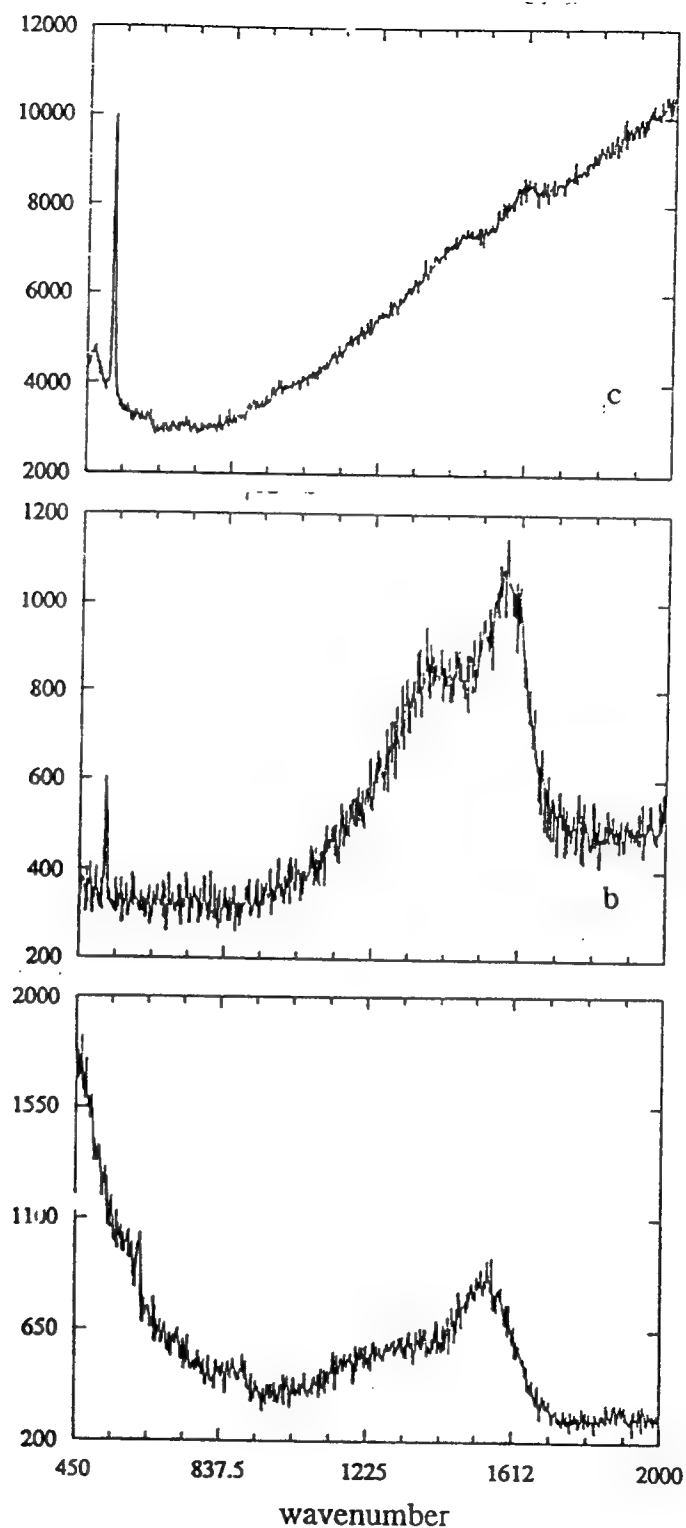
Figure 10. Raman spectra of carbon films formed by co-deposition of C_{60} (vaporized at 470° C) with high-energy nitrogen flux (beam voltage 700 V) on Si substrate at temperatures a - 300 K, b - 80 K, c - 18 K.

7. C$_{60}$ as a Lubricant (John L. Margrave and Associates)

In collaborative studies with one of the Houston Petrochemical Research Laboratories, we have evaluated C$_{60}$ as an additive to various motor oils, mineral oils and thermally stable organics but there has been no indication of enhanced lubricity. Among the negative factors observed were:

(1) Low solubility of C$_{60}$

(2) High vapor pressure of C$_{60}$

(3) Ease of oxidation of C$_{60}$

There does not appear to be any special advantage in using C$_{60}$ as a lubricant additive for standard motor oils.

8. Sublimation Pressures of a C$_{60}$/C$_{70}$ Solid Solution (John L. Margrave and Associates).

The transpiration method is one of the oldest and most versatile ways of studying heterogeneous equilibria involving solids and gases. In the transpiration experiment, an inert gas, a carrier, is passed over a condensed sample at a flow rate sufficiently low for equilibrium conditions to be established. The vapor of the sample is transported by the carrier gas to some point downstream from the sample and is collected and analyzed to determine the vapor pressures of components in the sample.

The quartz crystal microbalance (QCM) has also proved to be a useful tool in conjunction with the Langmuir free evaporation technique for measuring the vapor pressures of solids and liquids. Its high mass sensitivity allows the measurement of vapor pressures several decades lower than other methods. By employing a Knudsen effusion cell, this technique can be used with elimination of ambiguities relating to evaporation coefficients. Two major requirements have to be met: (1) the sticking coefficient of the vapor on the QCM must be near unity, and (2) the condensation of impurities from the sample container and the heating device must be negligible. A molecular beam, characteristic of the equilibrium vapors in the Knudsen cell, is formed by the species effusing from the cell orifice. This molecular beam can then be analyzed either with a mass spectrometer or with a deposition monitor (e.g., QCM).

The sublimation pressures in equilibrium with a polycrystalline C$_{60}$/C$_{70}$ solid solution have been measured with a quartz crystal microbalance (QCM) and by transpiration methods, in the temperature ranges 772-857 and 806-929 K, respectively.[27] The results from the two independent methods show good agreement. The solid solution was

found to have a total vapor pressure of 8.1×10^{-4} Torr at 800 K. It is estimated that the total vapor pressure of the C_{60}/C_{70} solid solution could reach 1 atm at ca. 1523 K. The analyses of the compositions of C_{60} and C_{70} in the solid and vapor phases also reveal that C_{60} is more volatile than C_{70}.

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III. STUDENTS, POSTDOCTORAL RESEARCHERS AND OTHER COLLABORATORS

(a) Students Who Have Completed Ph.D. Theses Involving C_{60} - Research

J. Michael Alford	(R. E. Smalley)
Norman Byrne	(M. A. Ciufolini)
L.P. F. Chibante	(R. E. Smalley)
J. Conceicao	(R. E. Smalley)
Scott Flanagan	(L. J. Wilson)
Michael Haley	(W. E. Billups)
Robert E. Haufler	(R. E. Smalley)
Sean C. O'Brien	(R. E. Smalley)
Chenyu Pan	(J. L. Margrave)
Z. Xiao	(J. L. Margrave)

(b) Other Researchers

Chad Fargason	(L. J. Wilson)	(currently pursuing a Ph.D. in mathematics at another university)
Michael Diener	(R. E. Smalley)	(working at Los Alamos)
Ting Guo	(R. E. Smalley)	(Ph.D. expected 5/95)
Eric Roche	(L. J. Wilson)	(currently pursuing a Ph.D. in chemistry at another university)
Andreas Thess	(R. E. Smalley)	(Ph.D. expected 5/97)
J. Zhang	(R. E. Smalley)	(received M.S. 5/94)

(c) Post-Doctoral Researchers

Dr. V. N. Khabashesku	(J. L. Margrave)
L. S. Wang	(R. E. Smalley)

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